

# SPECIFICATION

Docket No. 068267.000089

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN that we, Leland A. Hardcastle, Rex G. Sheppard, and David F. Dingus, citizens of the United States of America, residing in the State of Texas, have invented new and useful improvements in a

## PROCESS FOR MAKING POROUS GRAPHITE AND ARTICLES PRODUCED THEREFROM

of which the following is a specification:

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	<i>Sarah Garner</i>

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention:

The present invention relates generally to a process for the manufacture of porous solids and, more specifically, to a process for the manufacture of solid, high thermally conductive porous graphite artifacts and to improvements in the manufacturing process to enhance the properties of the artifacts so formed.

### 2. Description of the Prior Art:

This invention deals with carbon in its various forms and, particularly to artifacts formed of solid, porous graphite. Carbon fibers have been used commercially in industry for many years. Carbon fibers are known to exhibit extraordinary mechanical properties due to the unique graphitic morphology of the extruded filaments. Advanced structural composites have been created which advantageously exploit these properties by creating a disconnected network of graphitic filaments held together by an appropriate matrix.

Additionally, many of the current applications of carbon fibers have evolved from structural reinforcement applications to thermal or heat sink applications. For example, heat sinks have been utilized in the aerospace industry to absorb energy in applications such as missiles and aircraft where rapid heat generation is found. A number of heat absorption applications are also envisioned for the automotive industry.

These and other applications have stimulated research into novel reinforcements and composite processing methods for carbon materials. Acceptable materials must exhibit high thermal conductivity, low weight and a low coefficient of thermal expansion, among other requisite properties.

POCO Graphite, Inc., of Decatur, Texas, assignee of the present invention, has previously produced a line of specialty graphite materials that are routinely used in a wide range of highly technical and industrial applications. The following grades of porous graphites have been produced:

Grade:	ZXF-5Q	ACF-10Q	AXF-5Q	AXM-5Q	AXZ-5Q	TM	XT	FC
Typical Apparent Density (g/cc):	1.78	1.77	1.78	1.73	1.66	1.82	1.71	1.43
Thermal Conductivity (W/mK):	70	60	95	88	70	105	110	68

These high strength, fine grained isotropic graphites are easily machined by conventional machining methods. Their high strengths and small particle sizes allow the fabrication of complex components containing tight tolerances. The isotropic nature of the materials provides uniform electrical and thermal properties.

In spite of these advantages, the bulk thermal conductivities of these porous solid graphites have generally been below about 100 W/mK with apparent densities of 1.9g/cc and below. Efforts have been undertaken to produce porous graphite materials which exhibit even higher thermal conductivities in order to meet present and future commercial expectations.

Attempts have been made to improve upon the properties of solid graphite materials through the production of pitch based carbon "foam" materials. The apparent densities of such materials are lower than the apparent densities of the specialty graphites listed above. For the most part, the previously described prior art foam processes also resulted in foams which exhibited low thermal conductivities, generally less than about 58 W/mK.

One attempt to produce an improved carbon "foam" is described in now issued U. S. Patent No. 6,033,506, issued March 7, 2000 to Klett and in issued U.S. Patent No. 6,037,032, issued March 14, 2000, to Klett et al. The processes described in the Klett patents included steps which were less time consuming than the earlier known techniques for producing graphite foams and offered the

1 potential to lower production and fabrication costs. Perhaps more importantly, the Klett process  
2 claimed to produce carbon foams with thermal conductivities, generally greater than 58 W/mK.

3  
4 Although the Klett process was an improvement in pitch based carbon foaming processes,  
5 the Klett process utilized a static pressure during the formation of the green artifact (billet).  
6 Routinely, this static pressure selected was about 1000 psig. Graphite foams made in this manner  
7 have shown significant density gradients, generally ranging from about 0.25 g/cc at the top of a  
8 production billet to about 0.60 g/cc at the bottom of the billet and have exhibited voids and cracks.  
9 The claimed thermal conductivities have also not been achieved in some instances.

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11 Applicant's own improvements to the original Klett process, described in co-pending  
12 application serial number 09/862,560, filed May 22, 2001, entitled "Process For Making Carbon  
13 Foam Induced By Process Depressurization", use a "flash" method to induce boiling of the pitch  
14 precursor and produce porous graphite "foams" which have apparent densities ranging between 0.40-  
15 0.65 g/cc and thermal conductivities exceeding 58 W/mK without exhibiting voids or cracks as in  
16 the initial Klett process.

17  
18 A need continues to exist for graphite artifacts having even higher thermal conductivities,  
19 for example greater than 70 W/mK. A need thus exists for a solid, high thermally conductive porous  
20 graphite with an apparent density which exceeds that of the previously described graphite foams and  
21 with thermal conductivity characteristics greater than 70 W/mK.

22  
23 A need exists for an improved method for producing artifacts having these characteristics  
24 which artifacts are substantially free of density gradients, voids and cracks.

## SUMMARY OF THE INVENTION

It is one object of the present invention to provide a solid, high thermally conductive porous graphite which has a more uniform density gradient profile with less tendency to crack as a finished product as compared to the prior art.

Another object of the invention is to provide such a solid, porous graphite with an apparent density greater than about 0.678 g/cc.

Another object of the invention is to provide such a solid, porous graphite which has a thermal conductivity greater than 70W/mK.

In a specifically preferred process of the invention for producing a porous graphite, pitch is introduced into a mold, the pitch having a characteristic boiling point at a given pressure and for a given temperature. Air is then purged from the mold. The pitch is then pressurized between a preselected initial processing pressure and a relatively lower final processing pressure. The preselected initial pressure serves to increase the boiling point of the pitch above the boiling point at the final processing pressure. The pitch is heated while at the initial processing pressure to a temperature below the solidification point but above the boiling point which typically occurs at the final processing pressure. The pitch is then depressurized from the initial processing pressure to the final processing pressure while maintaining the process temperature above the typical boiling temperature at the final pressure to thereby produce a porous artifact. The porous artifact is heated to a temperature that solidifies and cokes the porous artifact to form a solid, porous carbon. The solid, porous carbon artifact can then be cooled to room temperature with simultaneous release of pressure. The porous carbon artifact then undergoes additional heat treatments to produce a porous graphite artifact having a thermal conductivity greater than 70 W/mK and a density greater than graphite foam.

1           The preferred solid, porous graphite artifacts so produced have a thermal conductivity greater  
2 than 150 W/mK and a density greater than 0.678g/cc. Artifacts having thermal conductivities greater  
3 than 150W/mK have been produced having densities in the range from 0.678g/cc and 1.5g/cc.

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5           Additional objects, features and advantages will be apparent in the written description which  
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## BRIEF DESCRIPTION OF THE DRAWINGS

**Figure 1** a graph of thermal conductivity in W/mK versus apparent density in g/cc for several prior art porous graphite materials as compared to the solid, high thermally conductive porous graphite of the invention.

Figure 1 is a graph of thermal conductivity in W/mK versus apparent density in g/cc for several prior art porous graphite materials as compared to the solid, high thermally conductive porous graphite of the invention.

## DETAILED DESCRIPTION OF THE INVENTION

In the discussion which follows, it is important to distinguish between graphite “foams” and “solid, porous graphite materials.” A “foam” will be defined herein to be a material having a relative density (RD) equal to or less than 0.3, i.e., being at least 70% porous. Using this definition, the artifacts prepared according to the method of the present invention have apparent densities greater than about 0.678 g/cc, relative densities greater than 0.3 and thus constitute “porous solids” rather than foams.

At a relative density (RD) above about 0.3, there is a transition from a cellular structure (foam) to one which is better thought of as a solid containing isolated pores (porous solid). RD can be defined as:

$$RD = p^{\circ} / p_s \text{ where } p^{\circ} = \text{density of cellular material}$$
$$p_s = \text{density of the material making the}$$
$$\text{solid cell walls (theoretical density)}$$

See: “*Cellular Solids, Structure and Properties*, Second Edition, Page 2, Lorna J. Gibson, Dept. of Materials Science and Engineering, MIT, Cambridge, MA 02139, USA, Michael F. Ashby, Dept. of Engineering, Cambridge, University, Cambridge, UK, Cambridge University Press, 40 W. 20<sup>th</sup> Street, New York, New York, 1988.

For example, a graphite foam with an apparent density of 0.50g/cc would have a  $RD = 0.50/2.26 = 0.22$  (where 0.5g/cc is the density of the cellular material and 2.26g/cc is the density of the graphite in the cell walls).



1 A sample with an apparent density of 0.678g/cc would have a  $RD=0.678/2.26=0.3$ , therefore  
2 any material produced that has an apparent density greater than 0.678g/cc will be a "solid"  
3 containing isolated pores according to the above definition. In the discussion of the invention which  
4 follows, reference will be made to both foams and solids, it being understood that the present  
5 invention is directed toward porous solids.  
6

7 One problem with previously produced "foamed" products was the presence of density  
8 variations from the top to the bottom of the production billet. The density variations in the end  
9 products were found to occur between the foaming and solidification steps of the prior art process  
10 while the foamed pitch was still in the liquid state. The liquid pitch tends to migrate due to gravity,  
11 thereby making the bottom of the production billet denser than the top portion of the billet.  
12

13 Applicant's previous application, serial number 09/862,560, concerned the discovery that,  
14 by heating the pitch under an increased pressure above 1000 psig, the process temperature can  
15 exceed the normal foaming point of the pitch without the pitch actually foaming, i.e., the thermal  
16 foaming point is raised. Holding the pitch at such a selected temperature allows the growth of  
17 mesophase domains within the pitch, thereby increasing the pitch's viscosity. Higher viscosities at  
18 this point in the process reduce the previously described migration problems.  
19

20 The present invention concerns the discovery that the apparent density of artifacts of the  
21 above type can be manipulated to produce "solid" graphites by processing at final pressures greater  
22 than 1000 psi and manipulating the final "boiling pressure". As a result of the higher and variable  
23 processing pressures, the apparent densities of the end products have been increased to greater than  
24 0.678 g/cc with thermal conductivities which exceed 150W/mK.  
25

26 Figure 1 shows a graph of thermal conductivity in W/mK versus apparent density in g/cc for  
27 several of the POCO specialty graphites as compared to the solid, high thermally conductive porous

graphite (HTCPG) of the invention. The thermal conductivity of the sample HTCPG in Figure 1 exceeds 250 W/mK.

In the process of the invention, a solid, porous graphite is produced by first placing pitch powder, granules or pellets into a mold or container with the desired final shape of the artifact to be produced. The pitch can be selected from among the mesophase pitches, isotropic pitches and mixtures thereof. The mesophase pitches include, for example, synthetic pitches, coal based pitches and petroleum based pitches. These pitch materials can be solvated if desired. The pitches can be introduced in the granulated, powdered or pelletized form. One example precursor material is the Mitsubishi ARA-24 mesophase pitch. A proper mold release agent or film can be applied to the sides of the mold to allow removal of the part. Preferably, a suitable liner, such as an aluminum foil liner is utilized. If the mold is made from pure aluminum, typically no mold release agent is necessary since the molten pitch does not wet the aluminum and thus does not stick to the mold.

The pitch may be desiccated to assist in removing any residual moisture. Following desiccation, the pitch is processed in a substantially oxygen-free environment to avoid oxidation of the pitch materials during heating. Preferably, the pitch is placed in a "HIP" furnace which has been evacuated to less than two torr. The HIP vessel is pressurized to a high initial pressure, e.g., 8000 psig, which increases the boiling point higher than the boiling point at the final processing pressure. The pitch is then heated to a temperature approximately 50 to 100°C above the softening point. For example, where Mitsubishi ARA-24 mesophase pitch is used, a temperature of 300°C is sufficient. After holding the pitch at 300°C for one hour, the pitch is heated from 300 to 450°C and held at 450°C for a predetermined amount of time to increase the viscosity of the liquid pitch.

The vessel is then depressurized from the initial processing pressure (8000 psig) to the final processing pressure, e.g., 2000 psig, while maintaining the temperature of the initial processing pressure. This depressurizing causes the liquid pitch to boil and generate porosity.

As will be explained in greater detail in the examples which follow, the boiling liquid is then heated to a temperature, e.g., 500°C, that solidifies the artifact in one or more steps. The temperature of the system can then be raised from 500°C to 600°C, or to a temperature sufficient to coke the pitch (about 500-600°C). This is performed at a rate no greater than about 5°C/min and preferably about 1°C/min. The final temperature is held at 600°C for about 2 hours and then the furnace power is turned off and cooled to room temperature. During the cooling cycle, pressure is released gradually to atmospheric conditions. Any remaining pressure is released at a rate of about 30 psi per minute. The artifact is then separated from the mold.

The artifact can be post heat treated to temperatures above 2000°C for conversion to graphitic structure, depending upon the pitch precursor. In general, mesophase pitch is graphitized significantly easier than isotropic pitches (coal derived or petroleum derived). The more graphitic the material, the higher the thermal conductivity of the resulting graphitic foam.

The specific steps followed in the process of the invention are summarized below:

1. A mold is filled with a pellet or powder form of mesophase pitch.
2. The pitch is then desiccated to assist in removing any residual moisture.
3. The pitch is placed into a Hot Isostatic Press (HIP).
4. The press is purged of air.
5. The pitch is pressurized to a high initial processing pressure, which increases the boiling point higher than the boiling point at the final processing pressure.
6. The pitch is heated to a temperature below the solidification point but above the liquid and boiling point which typically occurs if processed at the final processing pressure.
7. The pitch is depressurized from the initial processing pressure to the final processing pressure while maintaining the temperature which is above the pitch boiling point at the final processing pressure, thus producing a porous artifact.

- 1 8. The artifact is heated to a temperature that solidifies and cokes the porous artifact.  
2 9. The artifact is cooled to room temperature while allowing natural depressurization during  
3 cooling.  
4 10. The artifact is depressurized of any remaining pressure to atmospheric pressure.  
5 11. The artifact is removed from the HIP and mold.  
6 12. The artifact is then heat-treated to a sufficient temperature to completely carbonize the  
7 artifact.  
8 13. The artifact is then heat-treated to a sufficient temperature to graphitize the artifact.  
9

10 The process of the invention heats the pitch under an “increased pressure” which, in effect  
11 increases the thermal boiling point. That is, the process temperatures can exceed the “normal”  
12 boiling point of the pitch without the pitch actually boiling.  
13

14 In the first example which follows, the HIP was pressurized to 8000 psi as the “initial  
15 processing pressure.” This increased pressure will be understood to be an arbitrary number which  
16 could be anywhere in the range from about 4000 to 30,000 psig. In other words, assuming that a  
17 doubling of pressure generally increases boiling point by about 10°C, one could roughly estimate  
18 the boiling temperature of the pitch to be affected as follows:  
19

20	1000 psi	425°C
21	2000 psi	435°C
22	4000 psi	445°C
23	8000 psi	455°C

24  
25 Based upon this theoretical analysis, 8000 psi was selected as an acceptable “initial  
26 processing pressure” to achieve the desired pressurization induced boiling effect.  
27

1 The final processing pressure is also an arbitrary number which is generally in the range from  
2 about 1000 and 30,000 psig. As will be evident from the examples which follow the final processing  
3 pressure affects both the ultimate thermal conductivity and apparent density of the finished artifact.  
4 By employing final processing pressures which are greater than about 1000 psig, apparent densities  
5 are increased above 0.70g/cc and thermal conductivities exceed 250 W/mK.  
6

7 The following examples are intended to be illustrative of the process steps of the invention  
8 without being limiting:  
9

10 Example I

- 11 1. The mold is filled with a predetermined amount of pitch to give an appropriate foam height.
- 12 2.
- 13 2. The mold is placed in the HIP.
- 14 3. The HIP vessel is evacuated to <2 Torr with the vacuum being held for 15 minutes.
- 15 4. The vessel is pressurized to 8000 psig with nitrogen gas.
- 16 5. The pitch is heated from room temperature to 300°C at a rate of 3.5°C per minute.
- 17 6. The pitch is held at 300°C for 1 hour.
- 18 7. The pitch is heated from 300 to 450°C at a rate of 2.0°C per minute.
- 19 8. The pitch is held at 450°C for 1 hour. (This increases the viscosity of the liquid pitch).
- 20 9. The vessel is depressurized from 8000 to 2000 psig at a rate of 175 psi per minute while  
21 maintaining a temperature of 450°C. (At this stage, the liquid pitch begins to boil and  
22 generate porosity.)
- 23 10. The artifact is heated from 450 to 475°C at a rate of 2.0°C per minute.
- 24 11. The artifact is held at 475°C for 1 hour. (This is the point at which the artifact begins to set).
- 25 12. The artifact is heated from 475 to 500° C at a rate of 0.5 ° C per minute.
- 26 13. The artifact is held at 500°C for 30 minutes. (At this point, the artifact fully solidifies).
- 27 14. The artifact is heated from 500 to 600°C at a rate of 1.0°C per minute. (This is the stage at

which the artifact begins to coke.)

15. The artifact is held at 600°C for 2 hours.

16. The artifact is cooled from 600°C to room temperature at a rate of 2.0°C per minute.

17. The vessel naturally depressurizes during cooldown from 600°C to room temperature.

18. The remaining vessel pressure is released at a rate approximately 30 psi per minute.

19. The artifact is removed from the HIP and its mold.

20. The artifact is then heat treated to approximately 1000°C for carbonization.

21. The artifact is then heat treated to approximately 2800°C for graphitization.

Results: Thermal Conductivity ranged from 131 - 207 W/mK. Apparent Density ranged from .70 - .74 g/cc.

#### Example II

Same as Example I except:

9. The vessel is depressurized from 8000 psi to 3000 psi at a rate of 175 psi per minute while maintaining a temperature of 450°C.

Results: Thermal Conductivity ranged from 180 - 247 W/mK. Apparent Density ranged from .84 -.85 g/cc.

#### Example III

Same as Example I except:

9. The vessel pressure is held at 8000 psig while maintaining a temperature of 450°C.

Apparent Density was 1.10 g/cc.

#### Example IV

Same as Example I except:

8. The pitch is held at 450°C for 1.5 hours.

9. The vessel is depressurized from 8000 psig to 2800 psig at a rate of 260 psi per minute while maintaining a temperature of 450°C.

1 Results: Thermal conductivity ranged from 222 - 295 W/mK.

2 Apparent density ranged from 0.88 - 0.90g/cc.

3

4 An invention has been provided with several advantages. The process of the invention results  
5 in solid, high thermally conductive porous graphites having more uniform density gradient  
6 properties. The increased viscosity of the pitch during the processing operation reduces pore/bubble  
7 sizes within the ultimate porous artifact. Manipulation of the final process temperature allows  
8 greater control over pore size. Additionally, changing the hold times and temperature along with the  
9 various upper and lower pressure limits allows the production of a wider variety of porous graphite  
10 products. The porous solid graphites of the invention exhibit thermal conductivities which exceed  
11 70 W/mK, and generally range from about 90 - 300 W/mK with apparent densities ranging from  
12 about 0.678 g/cc - 1.5 g/cc.

13

14 While the invention has been shown in only one of its forms, it is not thus limited, but is  
15 susceptible to various changes and modifications without departing the sprit thereof.

16